

Layered Double Hydroxide Sorbents for Removal of Selenium from Power Plant Wastewaters

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Details of the Experimental Methods, Materials, and Procedures

1. Materials

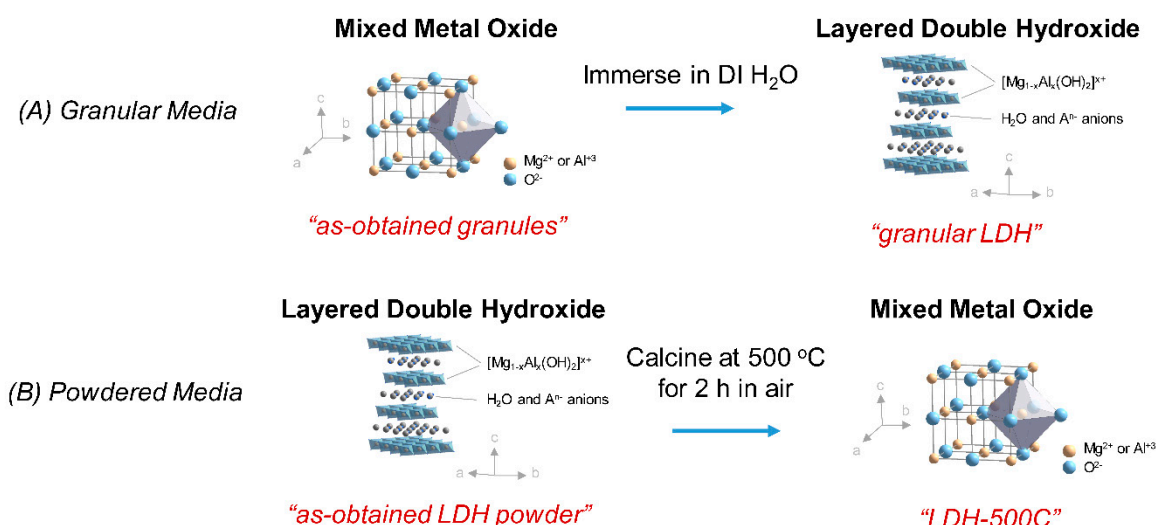
1.1. Materials Characterization

Sorbent materials were characterized as-received and after sorption tests. Powder X-ray diffraction (XRD) characterization was performed using monochromatic $\text{CuK}\alpha$ radiation ($\lambda=1.5405 \text{ \AA}$) with a Panalytical X'pert Pro MRD diffractometer with X'Celerator detector in Bragg-Brentano geometry operating at X-ray power of 45 kV/40 mA. The scanning step size was 0.01° , counting time was 20 sec, and 2θ range between $5 - 80^\circ$. Samples were pressed into a zero-background plate sample holder. Scanning electron microscopy (SEM) was performed with an FEI XL 30 field emission scanning electron microscope in secondary electron mode at 10 kV. The specific surface area was obtained using the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption at 77 K nitrogen (Micromeritics TriStar II 3020). Thermogravimetric analysis (TGA) was performed on a Setaram TG 92 at a heating rate of $5^\circ\text{C}/\text{min}$. Fourier transform infrared (FTIR) spectra of samples were collected on a Bruker IFS66V/S FTIR spectrometer (DTGS detector, KBr beam splitter, Glowbar source) using a diamond ATR sample module over the range of $400\text{--}4000 \text{ cm}^{-1}$ and 128 scans for background and sample spectra.

1.2. LDH Materials

Granulated mixed metal oxide media was obtained from Sasol Germany GmbH (PURALOX MG 63 HT-Granulate) with a reported media particle diameter of 1.46 mm, specific surface area of $188 \text{ m}^2/\text{g}$, total pore volume (Hg) of 0.626 mL/g , and loose bulk density of 0.51 g/mL . The reported composition was 38.3% Al_2O_3 and 61.7% MgO (2:1 Mg:Al atomic ratio). Prior to use in the column tests, the mixed metal oxide granules were rehydrated by immersing into de-ionized water to form the granular LDH media (Scheme S1a). Characterization of the physical properties of this media by XRD, SEM, and FTIR as well as the adsorption properties in de-ionized water solutions containing selenium can be found in our previous studies [1,2].

Powdered layered double hydroxide (LDH) material was obtained from Sigma-Aldrich (Hydrotalcite-synthetic, product no. 652288). The XRD pattern of the as-received LDH powder (Figure S1a) was a good match to the reference pattern for $(\text{Mg}_{0.667}\text{Al}_{0.333})(\text{OH})_2(\text{CO}_3)_{0.167}(\text{H}_2\text{O})_{0.5}$ (PDF 01-089-0460) [3], indicating that the LDH powder had a rhombohedral crystal structure (space group R-3m) with interlayer carbonate and water molecules. The as-obtained LDH powder was hydrophobic and could not be dispersed into water unless it was calcined. XRD performed on the LDH powder calcined at 500°C in air for 2 h (LDH-500C, Scheme S1b) showed the formation of the periclase structure associated with the removal of interlayer water and carbonate anions (Figure S1a) [4,5]. The XRD pattern of LDH-500C was also very similar to that for the as-obtained mixed metal oxide granules [1]. SEM imaging showed that the as-obtained powder consisted of particles about 500 nm in size and remained similar in morphology and size after calcination (Figure S1b). Calcination of the LDH powder was effective for increasing the surface area, from $7 \text{ m}^2/\text{g}$ for the as-obtained powder to $179 \text{ m}^2/\text{g}$, according to the BET measurements.



Scheme S1: Structure of as-obtained granules and powder with processing conditions. "Mixed metal oxide" refers to the Mg/Al oxide solid solution with periclase structure. Red text refers to the names used to refer to the samples throughout this work.

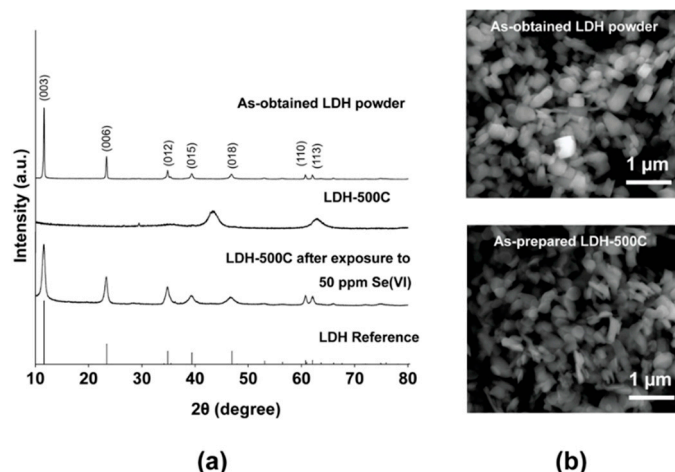


Figure S1: XRD and SEM characterization of LDH-500C **(a)** XRD patterns of layered double hydroxide (LDH) materials: as-obtained LDH powder, LDH powder after calcination at 500 °C for 2 h (LDH-500C), and after LDH-500C was used in jar test to remove 50 ppm Se(VI) from DI water. The pattern for $(\text{Mg}_{0.667}\text{Al}_{0.333})(\text{OH})_2(\text{CO}_3)_{0.167}(\text{H}_2\text{O})_{0.5}$ from PDF 01-089-0460 is shown as reference. **(b)** SEM images of as-obtained LDH powder and as-prepared LDH-500C.

FTIR spectroscopy of the as-obtained LDH powder (Figure S2, black trace) revealed bands associated with interlayer carbonate anions at 1354 cm^{-1} [6,7] lattice vibrations of Mg,Al-oxide octahedral sheets at 445 cm^{-1} , Mg/Al-OH translations at 550 cm^{-1} , 664 cm^{-1} , and 775 cm^{-1} , and Al-OH deformation at 943 cm^{-1} [7–9]. The FTIR spectrum of LDH-500C (Figure S2, red trace) showed that these characteristic bands disappeared after the heat treatment, consistent with dehydroxylation and collapse of the layered-structure during calcination. The FTIR spectrum for LDH-500C was also very similar to that for the as-obtained mixed metal oxide granules (Figure S2, blue trace), justifying the use of LDH-500C as a surrogate for the granules in jar tests.

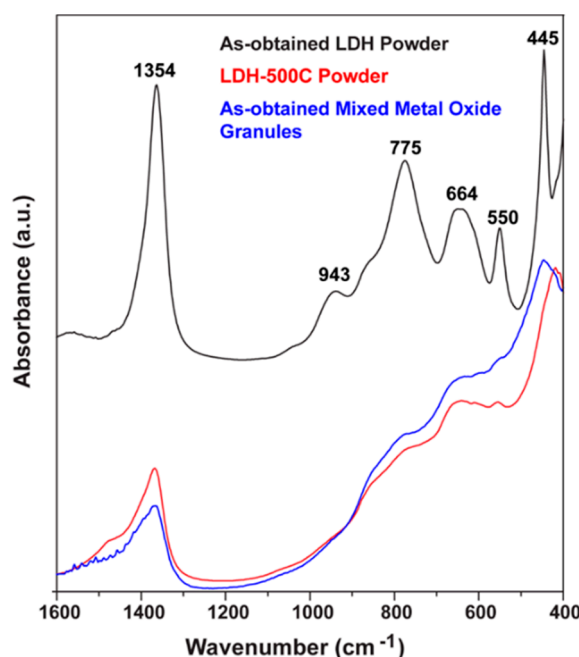


Figure S2: FTIR spectra of LDH-500C. FTIR spectra of: as-obtained LDH powder, LDH powder after calcination at 500 °C for 2 h (LDH-500C), and as-obtained mixed metal oxide granules.

2. Jar Testing Procedures

2.1. Synthetic water samples

Synthetic water samples for jar tests (adsorption isotherms and kinetic testing) were prepared from ultrapure de-ionized (DI) water (18.2 MΩ, pH 5.5) spiked with selenium. Stock solutions (1000 ppm) of selenate, Se(VI), and selenite, Se(IV), were prepared by dissolving Na₂SeO₄ (Sigma-Aldrich, product no. 71948-100G, purity ≥ 98.0%) or NaHSeO₃ (Sigma-Aldrich, product no. S5261-25G, purity ≥ 98) into DI water.

2.2. Analysis of selenium concentrations in water

Water samples were filtered using a 0.2 micron Isopore track etched polycarbonate membrane in a Pall syringe filter. Then, 2% nitric acid was added to the filtered sample solution for analysis of total selenium concentrations with inductively coupled plasma optical emission spectroscopy (ICP-OES, ICAP-6300, Thermo Co., USA) or inductively coupled plasma - mass spectrometry (ICP-MS, iCap Q quadrupole, Thermo Co.) for samples with low levels of selenium. For spiked solutions containing concentrations > 20 ppm selenium, the water was diluted 50X prior to ICP-OES analysis.

2.3. Equilibrium isotherms

Adsorption isotherms were conducted using 1 g/L of LDH-500C in 250 mL DI water (pH 6) spiked with Se(VI) solutions ranging from approximately 5 - 50 ppm. The dry LDH-500C powder was added directly to the test waters. The samples were agitated for 22 h on a compact digital mini rotator (Thermo Scientific, Catalog no. 88880025) in order to reach equilibrium. The experimental data plotted are the averages of duplicate runs. The error was calculated using the standard deviation from the mean. The Langmuir model was applied to describe the adsorption behavior at equilibrium [10]. The Langmuir isotherm can be expressed as shown in Equation 1 [11], where C_e (ppm) is the concentration of Se(VI) at equilibrium; Q_e (mg/g) is amount of Se(VI) adsorbed per mass of LDH-500C at equilibrium for each C_e ; Q_{max} (mg/g) is the maximum amount of Se(VI) adsorbed; and K (L/mg) is the equilibrium constant.

$$Q_e = \frac{Q_{max} K C_e}{1 + K C_e} \quad (1)$$

The Langmuir equation can also be expressed as shown in Equation 2,

$$C_e/Q_e = 1/Q_{max} K + C_e/Q_{max} ; \quad (2)$$

therefore, the slope of the Langmuir plot is $1/Q_{max}$ and the intercept is $1/Q_{max} K$. The isotherm results shown in Figure 1 showed a good fit to the Langmuir model. The linear fit of the experimental data was $y = 0.0151x + 0.1089$, where $y = C_e/Q_e$ and $x = C_e$, with a correlation coefficient value of $R^2 = 0.9927$.

2.4. Selenium removal efficacy from spiked power plant waters

To assess the sorbent efficacy for Se(VI) removal from power plant wastewaters, batch tests were performed using LDH-500C at concentrations ranging from 1 - 5 g/L. Due to the low-ppb natural levels of selenium in the as-obtained water samples (Table S1), jar tests were performed in wastewater samples spiked with 0.2 ppm Se(VI). The sorbents were added to the water solutions and stirred at a constant speed with a magnetic stirrer, with sampling performed after different time periods. The removal of Se(VI) from spiked W1 (well water) using different dosages of LDH-500C is shown in Figure S3.

Table S1: pH and Se levels in power plant wastewater jar tests. The pH values were obtained immediately after sampling (July 2014) and ranged from 6.88 to 8.42. Total Se concentrations were determined using ICP-MS.

Water	pH	Se (ppb)
C2	7.95	BRL ¹
C4	6.88	2.94
W1	7.71	2.72
W2	7.57	5.75
D	8.42	2.37

¹ Below reporting limit

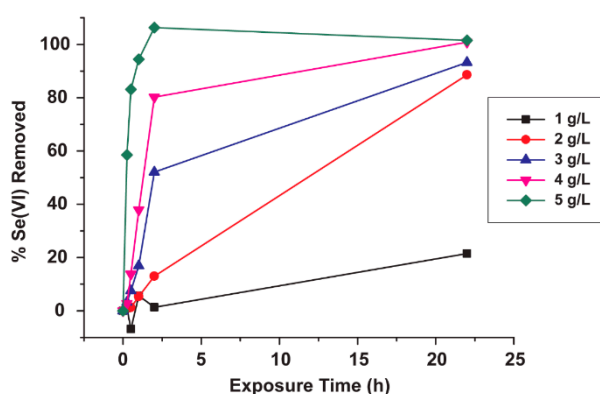


Figure S3. Effect of LDH dosage on Se(VI) removal. Removal of 0.2 ppm selenate from spiked W1 water using different dosages of LDH-500C

3. Small-Scale Column Testing Procedures

For the small-scale column testing, the as-obtained mixed metal oxide granules were gently ground into small particles using a mortar and a pestle. Particles ranging in size between 250–500 μm were obtained using sieves (mesh No. 35 and No. 60). The granules were then immersed in DI water to remove any air before packing, allow for media expansion, and to re-hydrate the media. Note!

Failure to re-hydrate the mixed metal oxide granules prior to its introduction into the column can lead to a great deal of heat generation once water flow is initiated and this should be avoided to avoid damage to column equipment.

The glass column (1.1 cm diameter, 30 cm height) was obtained from Ace Glass (no. 5820-06) along with the Teflon endcaps and connectors (Figure S4). The sorbent bed was packed in the middle one-third of the column. Glass wool (Sigma-Aldrich) was placed above and below the media bed as well as in both ends of the column as a support and to retain all of the sorbent media inside the column. Glass beads (Ace Glass, 5 mm diameter, no. 8035-07) were placed on either side of the glass wool to better disperse the influent flow. Prior to use, the glass wool and glass beads were heated at 500 °C for 1 h in air to remove any contaminants and then stored in DI water. After packing the column, backwashing was performed using DI water to remove fine particles in countercurrent (upflow) mode until the effluent water ran clear. The bed height was approximately 50 mm and bed volume (calculated from the mass of media used and its density) was 4.75 cm³. A peristaltic pump (NE-9000G, New Era Pump Systems) was used to set the flow rate to 0.158 mL/min to achieve the desired empty-bed contact time (EBCT) of 30 min. The cooling tower blowdown water provided by Salt River Project was sampled in March 2017 (cooling tower 5 at Santan Generating Station). The as-obtained water was connected to the influent line and pumped in up-flow mode into the column. Samples of the column effluent were taken approximately every 2 hours and the total selenium and sulfate (as S) were determined from acidified samples using ICP-MS. After the column test, the sorbent was removed and dried at 50 °C for one week and the mass of 5.38 g was measured for calculation of the selenate capacity.

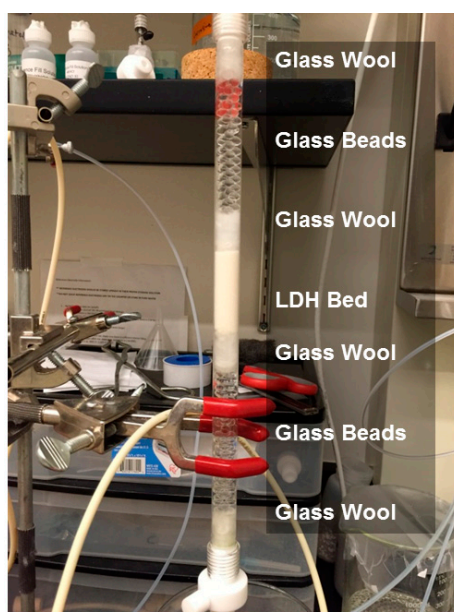


Figure S4: Photograph of small-scale column setup

The breakthrough curves were analyzed as described by ref. [12] and the results are presented in Table S2. The exhaustion capacity Q_e of the sorbent for Se was calculated using Equation 3 where C_0 (µg/L) is the initial Se(VI) concentration in the influent; C (µg/L) is the Se(VI) concentration in the effluent after leaving the column; m (g) is the dried sorbent bed mass in the column; and V_e is the water volume (L) that was treated at exhaustion (values for S were similarly determined).

$$Q_e = \frac{\int_{V=0}^{V=V_e} (C_0 - C) dV_e}{m} \quad (3)$$

The adsorbent exhaustion rate (AER) was estimated using Equation 4 and V_{1g} , the volume of water (L) that can be treated with 1 g of sorbent was taken as the inverse of the AER.

$$AER = \frac{m}{V_e} \quad (4)$$

Table S2. Comparison of small-scale column test results. The same granular LDH was used in the same size column for removal of selenium from groundwater and cooling tower (CT) blowdown with same EBCT.

Water	$C_o(\text{Se})$, $\mu\text{g/L}$	$C_o(\text{S})$, mg/L	$[\text{S}]/[\text{Se}]$	$Q_e(\text{Se})$, $(\mu\text{g/g})$	$Q_e(\text{S})$, (mg/g)	Reference
Groundwater	1.75	37	21,000	0.65	18	[1]
CT Blowdown	2.67	187	70,000	0.55	42	This work

4. Evaluation in Column Testbed

The testbed comprised of three serially connected 2" (5.08 cm) diameter columns with total height of ~200 cm (26 inches or 66 cm for each column) and was operated in up-flow mode with less than 30% bed expansion (down-flow mode was found to cause significant head loss and pressure build-up, possibly due to attrition of the granular media). Each column was equipped with a 60 mesh (250 μm) screen at the bottom to contain the media. The bed volume of each column was calculated to be 668 cm^3 , with 375 g of granular LDH media filling about 50% of the height of the column (~13" or 33 cm). The total bed volume for the three columns was estimated as 2,007 cm^3 with total sorbent mass of 1,264 g. Prior to loading into the columns, the as-obtained granules were immersed into de-ionized water to re-hydrate the media and prevent excessive heat generation upon initiation of water flow.

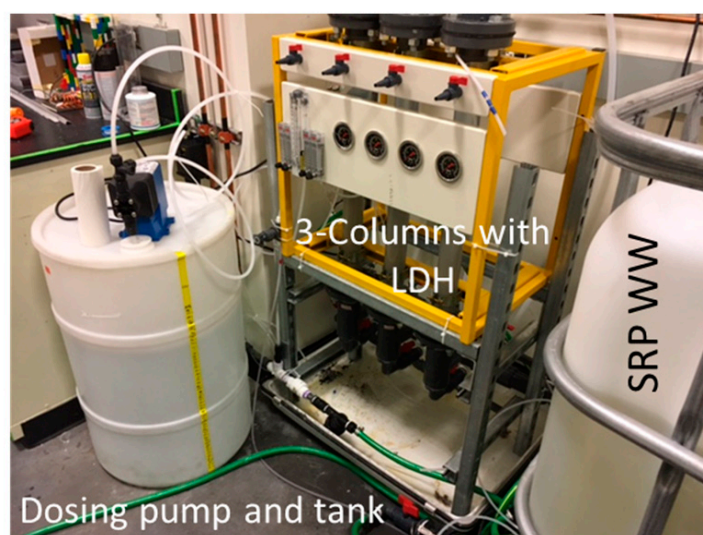


Figure S5: Photograph of testbed. The source wastewater (WW) is shown in the tote on the right.

Water samples from Santan Generation Station were provided by Salt River Project in 330 gallon totes. The discharge water was sampled on June 7, 2017 and consisted of commingled wastewater from the wastewater ponds of the plant (corresponding to point D in Figure 2a). The blowdown water

(from cooling tower 5) was collected (August 17, 2017) after the water had been treated with sodium bisulfite for de-chlorination. The makeup water for the cooling tower blowdown was surface water. The concentration of select ions was determined using ICP-MS from the influent feed samples and the results are shown in Table S3.

The column test was performed using a hydraulic loading rate of 3 m/hr (1.2 gpm/ft²), EBCT of 20 min, and operated continuously to ~1,000 bed volumes of operation (15 consecutive days) without stopping except for backwashing. The pressure of each column was monitored using pressure gauges (0–60 psi, AMI) and backwashing was performed whenever the pressure built up to 10 psi in order to eliminate fine particles. Two samples per day were collected for the effluent water coming out of the last column (column 3) and analyzed using ICP-MS. The influent feed was also sampled at the same time. The flow rate (rotameter, 50–700 mL/min, Dwyer), pH, conductivity, temperature (multi-meter, model HI991301, Hanna), UV-245 absorbance (DR5000 spectrophotometer, Hach; after filtration with 0.45 µm filter), and turbidity (DRT-15CE, HF Scientific) were also monitored each day. Select effluent samples were also analyzed for alkalinity using a Hach Alkalinity test kit with digital titrator (model AL-DT, product no. 2063700).

Table S3. Water composition of wastewaters treated in the testbed evaluation of LDH. Concentrations were determined with ICP-MS and shown as the average level in the influent during the column test with standard deviation.

Water Type	CT Blowdown	Plant Discharge
pH	7.55 ± 0.20	7.86 ± 0.09
Se (ppb)	1.22 ± 0.09	1.28 ± 0.02
S (ppm)	175.14 ± 8.38	110.43 ± 3.69
[S]/[Se]	~144,000	~86,000
Mg (ppm)	48.91 ± 0.73	37.21 ± 1.90
Al (ppb)	3.23 ± 1.57	3.77 ± 1.10
P (ppb)	794.25 ± 51.28	485.89 ± 25.78
Cr (ppb)	9.27 ± 0.50	7.25 ± 0.25
Cu (ppb)	6.12 ± 0.89	3.52 ± 0.73
As (ppb)	8.47 ± 0.25	8.22 ± 0.24
Zn (ppb)	59.76 ± 7.64	14.83 ± 5.47
Na (ppm)	509.12 ± 15.16	Not measured
K (ppm)	13.85 ± 0.78	Not measured
Ca (ppm)	139.61 ± 9.6	120.53 ± 4.21

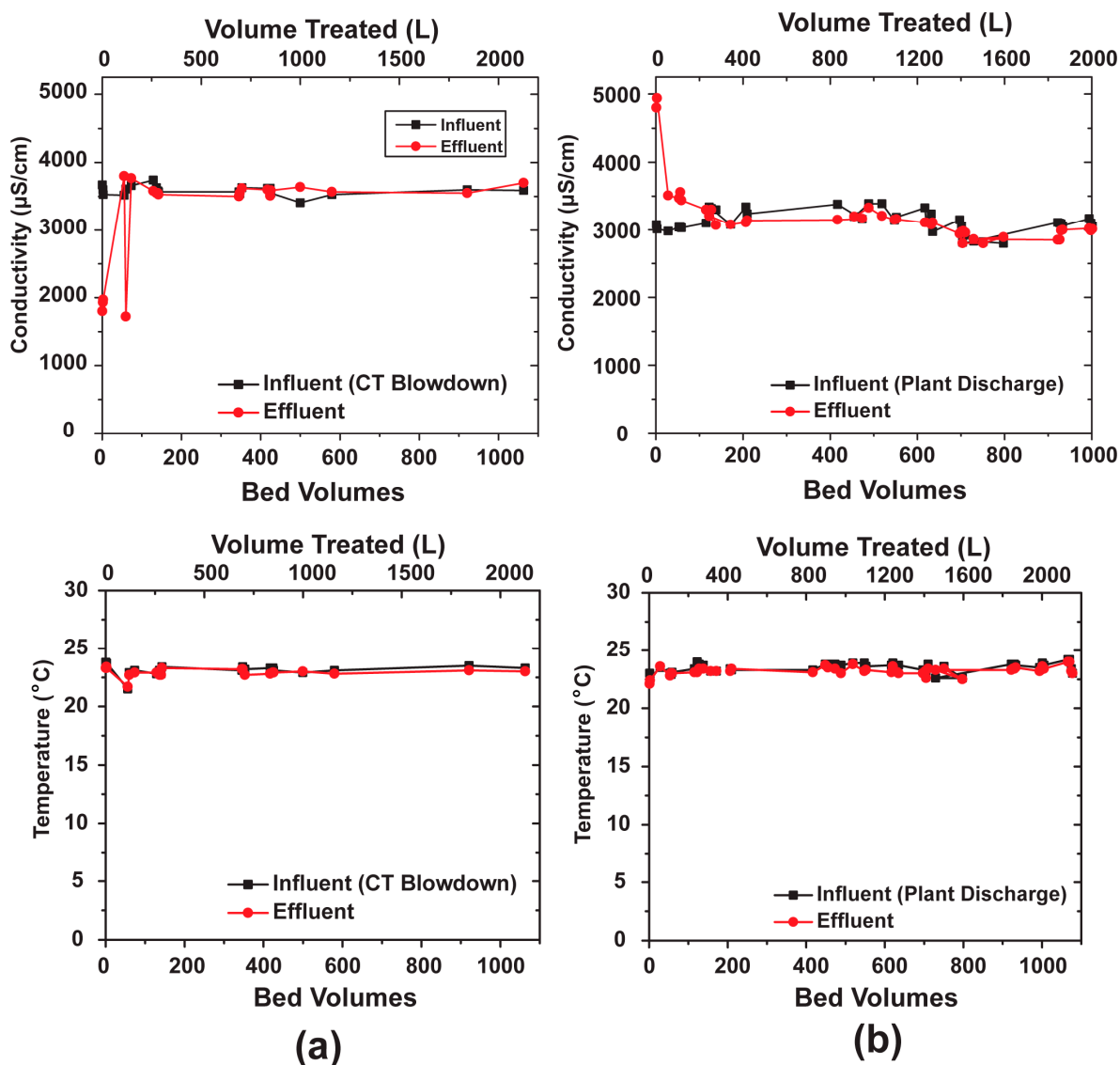


Figure S6. Conductivity and temperature of influent and effluent from the testbed studies. **(a)** CT blowdown water, **(b)** plant discharge wastewaters.

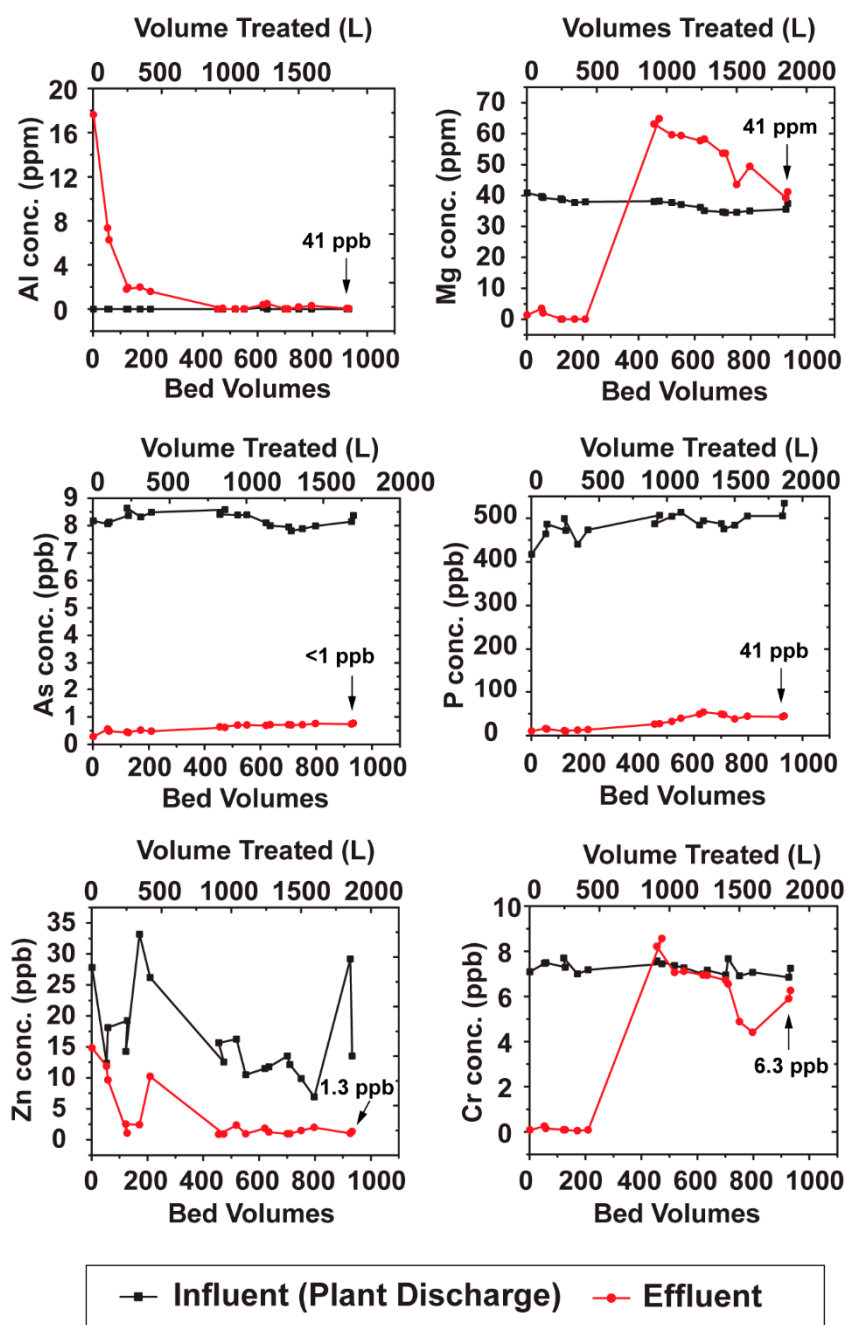


Figure S7. Concentration of select ions in plant discharge wastewater influent and effluent from testbed studies.

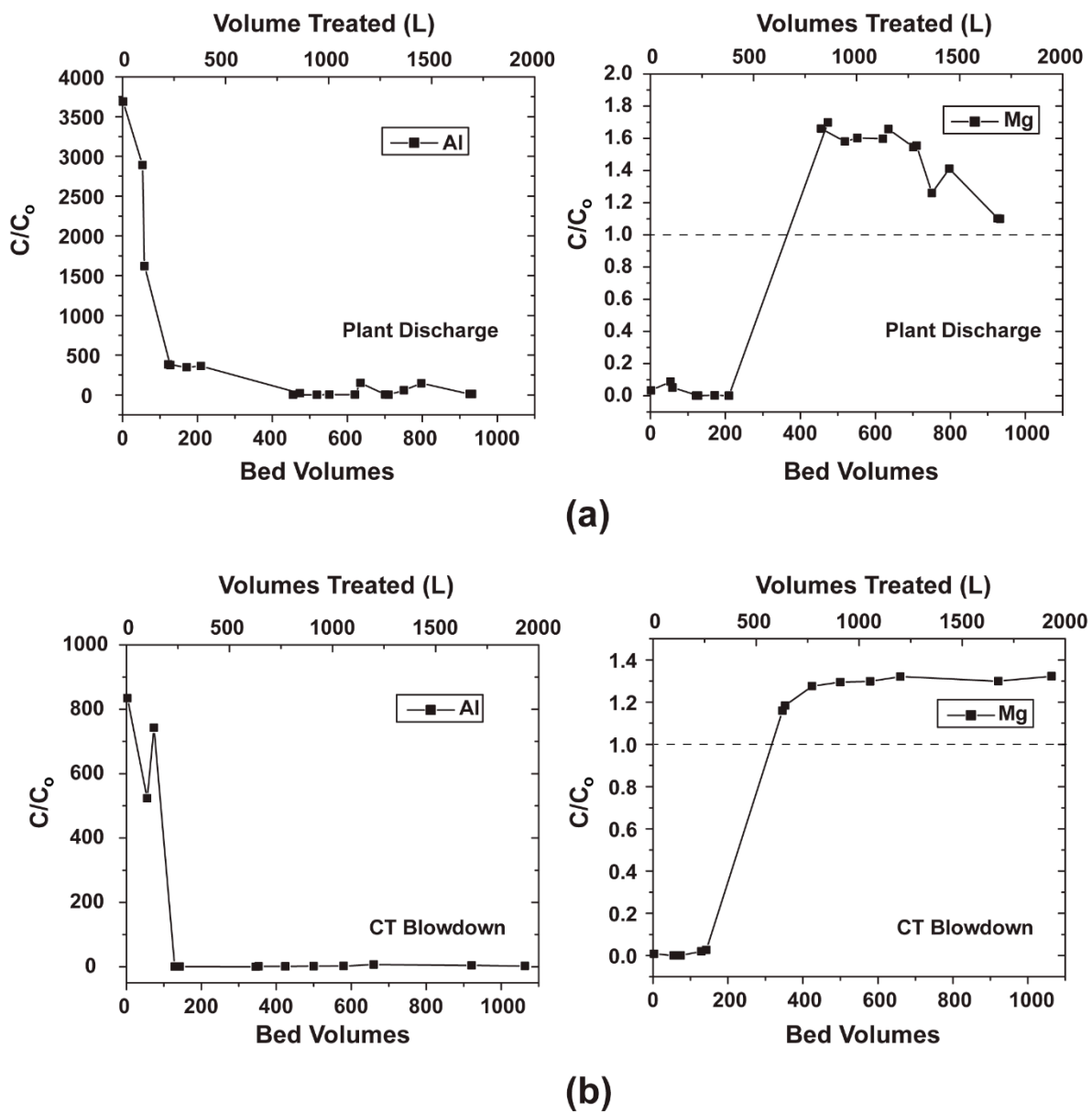


Figure S8. Ratio of effluent to influent (C/C_0) levels for Al and Mg in testbed. (a) Plant discharge and (b) CT blowdown water.

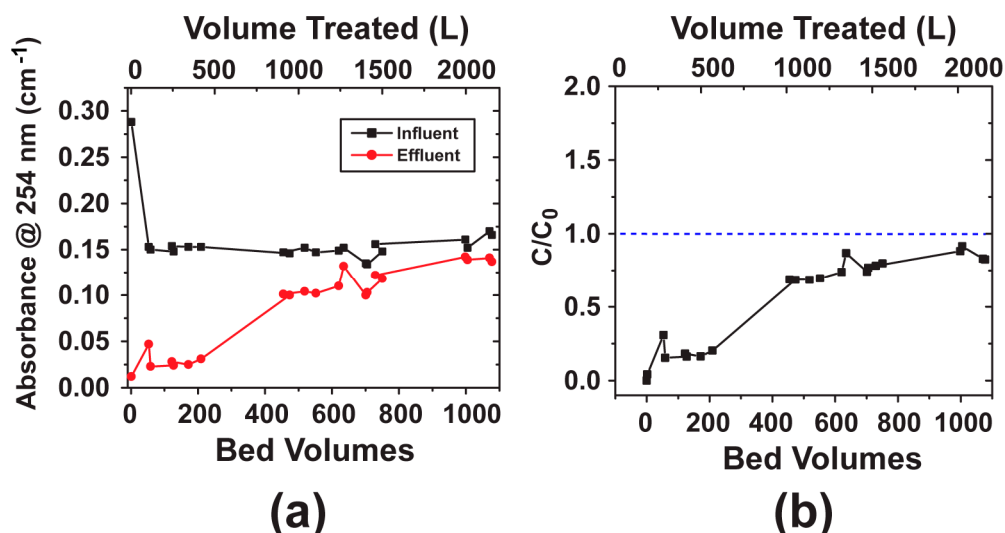


Figure S9. UV-vis absorbance results from testbed. (a) UV-vis absorbance at 254 nm in influent and effluent of plant discharge column test, (b) ratio of effluent to influent (C/C_0) levels for absorbance at 254 nm.

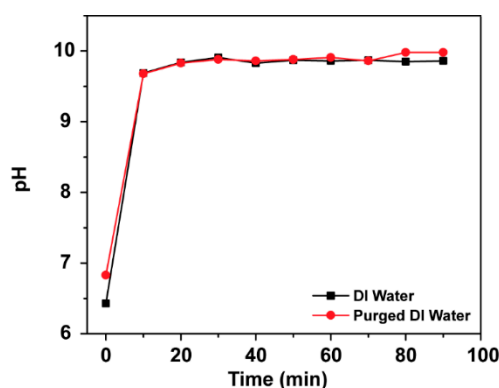


Figure S10. Jar test study monitoring pH change. Change in pH after immersing as-obtained mixed metal oxide granules (1 g/L) into DI water and DI water purged with N₂. In both cases, the pH rapidly increased to above 9.5 within 10 minutes.

Table S4. Alkalinity (in mg/L) for effluent samples from CT blowdown column test as determined using titration.

Bed Volumes	Total Alkalinity	Hydroxide	Carbonate	Bicarbonate
140.5	160	40	120	ND ¹
144.5	140	20	120	ND ¹
1077	78	ND ¹	ND	78

¹ Not detected at the reporting limit (10 mg/L).

5. Pilot-scale testing

The pilot unit was built by and leased from Canyon State Filtration (Sedona, AZ). The skid contained four identical columns 3" in diameter and 6" high with 4" of underlayment (Figure S11).

Each column was equipped with an inline flow meter to visually set the required flow rate. For this test, only one column was utilized. A gravel layer consisting of Colorado Silica Sand™ (Premier Silica) was used to support the bed in each column. The desired bed volume (70% of the height of the column) was 0.17 ft³, so 6.74 pounds (3,060 g) of granular LDH media was used in the column. The bed volume was 1.27 gal (4.8 L).



Figure S11. Photograph of pilot skid.

Cooling tower blowdown was connected directly to the column and the bed was backwashed to remove fine particles. Then, the flow rate was set to 0.043 gal/min (0.161 L/min) for a desired EBCT of 30 min with the water entering from the top of the column. A booster pump was used since the line pressure in the cooling tower discharge lines was negligible. Analysis of the metal composition of the influent feed water (sampled November 4, 2016) was performed using ICP-MS and the results are shown in Table S5.

Additional water analyses of the anion composition of the influent feed water and effluent after 77 BVs were performed by TestAmerica Phoenix (4625 East Cotton Blvd, Suite 189, Phoenix, AZ 85040). Nitrate (as N), orthophosphate (as P), chloride, sulfate, bromide, and fluoride concentrations were determined using ion (anion) chromatography (Method 300.0, "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, March 1983 and subsequent revisions). Bicarbonate was analyzed using the alkalinity method SM 2320B, total dissolved solids (TDS) was determined using method SM 2540C, and total residual chlorine was determined using method SM 4500 Cl G ("Standard Methods for the Examination of Water and Wastewater").

Table S5. Water composition of test waters for pilot test. Concentrations determined with ICP-MS from the influent levels obtained during sampling.

Water Type	CT Blowdown
pH	6.99
Se (ppb)	2.74
S (ppm)	214
[S]/[Se]	~78,000
Al (ppb)	4.63
Cr (ppb)	3.28
Mn (ppb)	6.97
Cu (ppb)	3.28
As (ppb)	16.70
Zn (ppb)	180.82
Fe (ppb)	114.65
Mg (ppm)	73
Ca (ppm)	237



Figure S12. Photographs of biological growth in pilot column.

6. Post-Mortem Materials Characterization

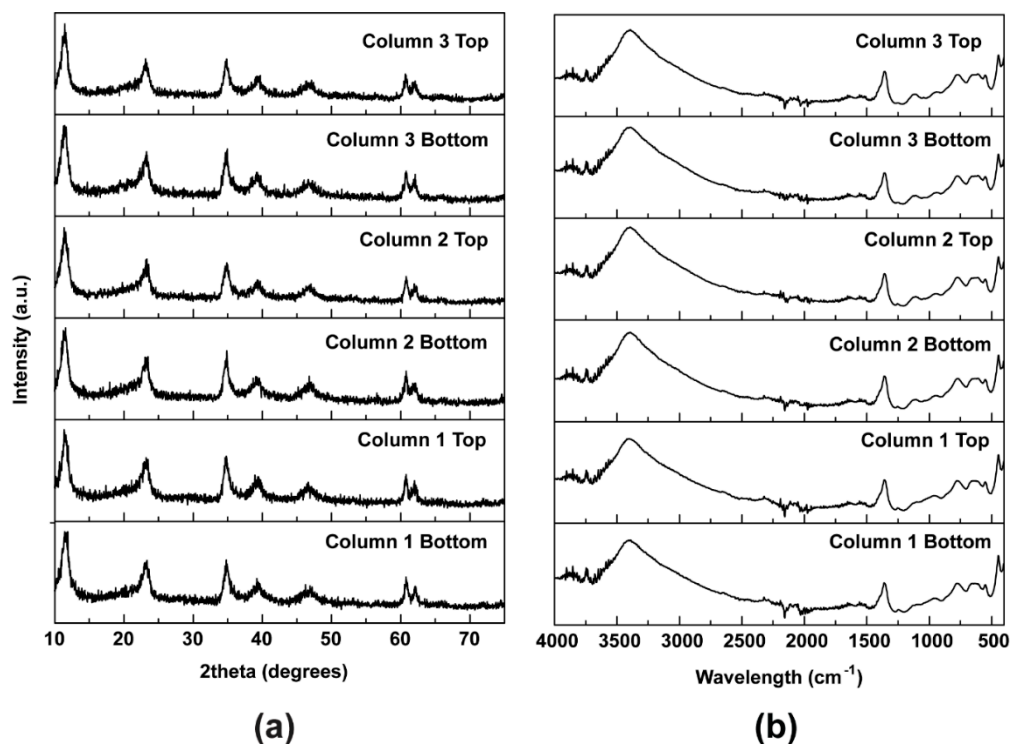


Figure S13. XRD and FTIR analysis of exhausted testbed media. (a) XRD patterns and (b) FTIR spectra of exhausted LDH media taken from different parts of the testbed.

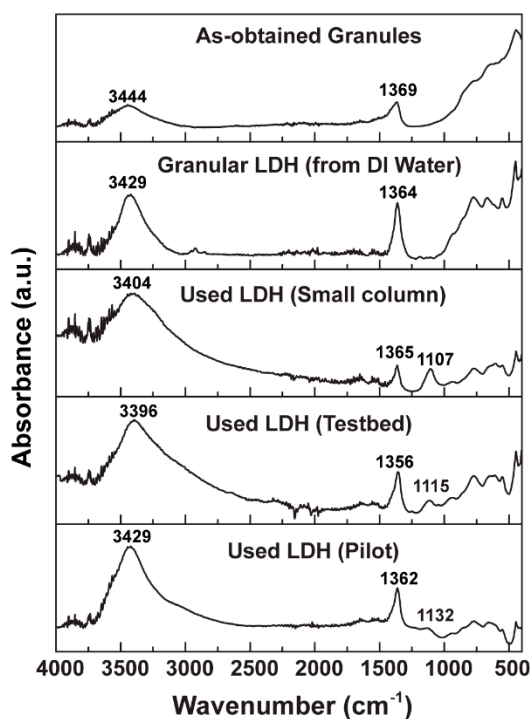


Figure S14. Wide-range FTIR comparison. Comparison FTIR spectra over a wide range for as-obtained granules, granular LDH formed after immersion of as-obtained granules into de-ionized (DI) water purged with N₂, and used LDH granules from the different column tests. For a zoomed-in view of the spectra in the region of 1600–400 cm⁻¹, see Figure 9.

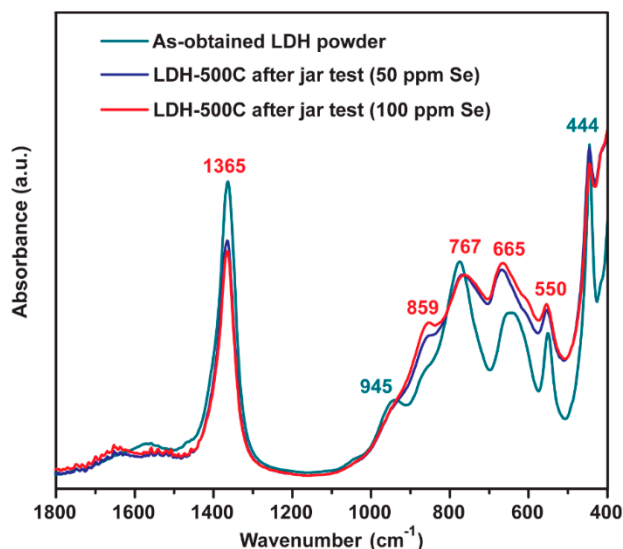


Figure S15. FTIR characterization of selenate adsorption onto LDH. LDH-500C was exposed to DI water solutions containing 50 ppm (blue trace) and 100 ppm (red trace) selenate (from Na_2SeO_4) followed by drying. The band associated with the $\nu(\text{Se-O})$ vibrations of $\text{Se(VI)-O-Mg,Al-LDH}$ complexes [8] was observed at 859 cm^{-1} after exposure to selenate. Interlayer carbonate anions can be identified by the band at 1365 cm^{-1} [6,7]. Bands at 444 cm^{-1} are assigned to the lattice vibrations of Mg,Al-oxide octahedral sheets, at 550 cm^{-1} , 665 cm^{-1} , and 767 cm^{-1} to Mg/Al-OH translations, and at 945 cm^{-1} to Al-OH deformation [7–9].

7. LDH stability tests

As-obtained granules (0.2 g) were suspended in 200 mL DI water and agitated using an orbital shaker (set to 150 rpm) for 24 h. The solids were removed from the water with a $0.2\text{ }\mu\text{m}$ syringe filter followed by centrifugation (15 min at 14,000 rpm). The solution was then analyzed using ICP-MS. Similar jar test experiments were performed using solutions of DI water containing 1 ppm Se(VI) , DI water with pH adjusted to 12 using NaOH, and DI water with pH adjusted to 12 using NaOH containing 1 ppm Se(VI) .

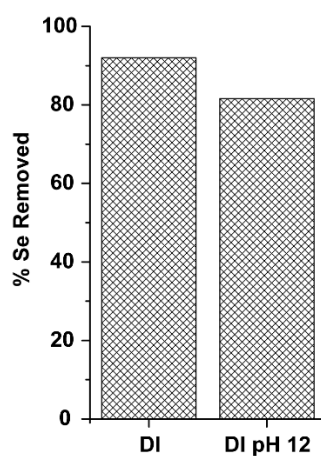


Figure S16. Effect of pH on Se(VI) removal. Percentage of 1 ppm Se(VI) removed from DI water after 24 h using as-obtained granules at 1 g/L dosage from DI water and DI water adjusted to pH 12 with NaOH.

8. Regeneration of LDH media

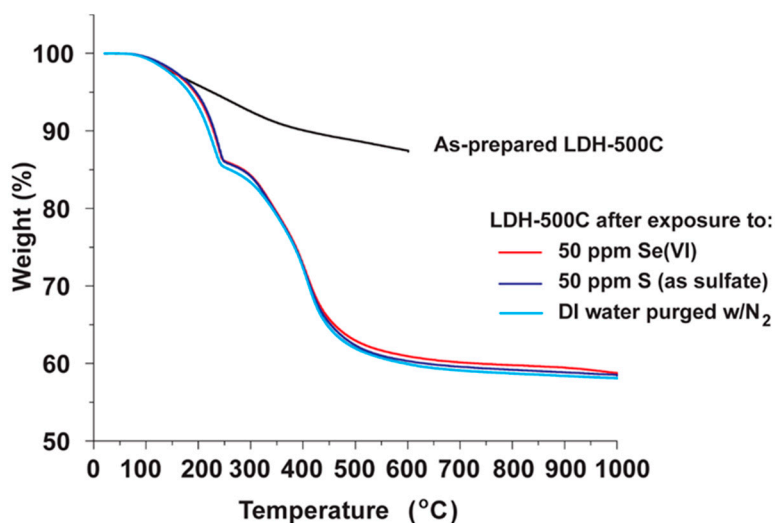


Figure S17. TGA data of different LDHs. Samples were as-obtained LDH powder, as prepared LDH-500C; LDH-500C after exposure to 50 ppm selenate, 50 ppm sulfate, or DI water purged w/N₂. The first weight loss region is attributed to removal of interlayer water molecules, while the second is from removal of interlayer anions.

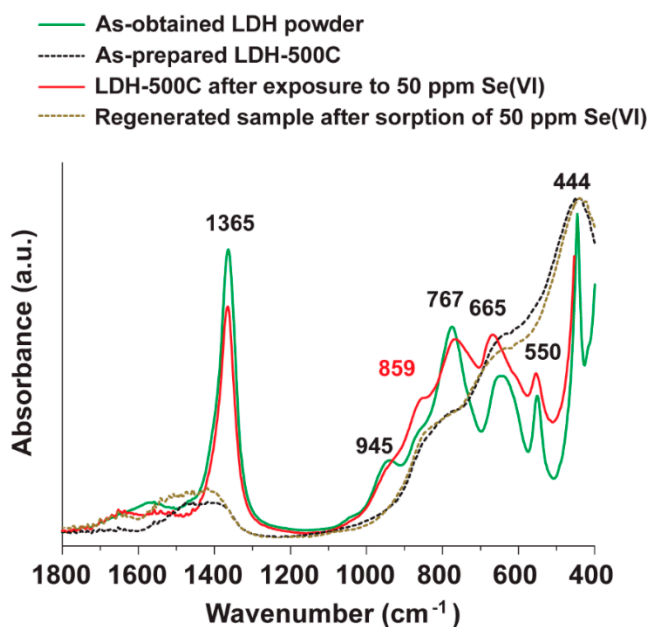


Figure S18. FTIR spectra of different LDHs. Samples were as-obtained LDH powder, as-prepared LDH-500C (i.e., LDH powder after calcining at 500 °C), LDH-500C after exposure to 50 ppm Se(VI), and regenerated LDH-500C sample after exposure to 50 ppm Se(VI) and calcination at 550 °C.

Supplementary Materials References

1. Li, M.; Farnen, L. M.; Chan, C. K. Selenium Removal from Sulfate-Containing Groundwater Using Granular Layered Double Hydroxide Materials. *Ind. Eng. Chem. Res.* **2017**, *56*, 2458–2465, doi:10.1021/acs.iecr.6b04461.
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